UNIVERSITY OF ZAGREB
FACULTY OF MECHANICAL ENGINEERING
AND NAVAL ARCHITECTURE

BACHELOR'S THESIS

Davor Stjelja

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SVEUČILIŠTE U ZAGREBU
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ZAVRŠNI RAD

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UNIVERSITY OF ZAGREB
FACULTY OF MECHANICAL ENGINEERING
AND NAVAL ARCHITECTURE

MEASUREMENT OF HEAT CONDUCTIVITY OF THE LIQUIDS

Supervisor: Student:

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Zagreb, 2014

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FAKULTET STROJARSTVA I BRODOGRADNJE

MJERENJE TOPLINSKE PROVODNOSTI KAPLJEVINA

Mentor: Student:

Prof. dr. sc. Davor Zvizdić, dipl. ing. Davor Stjelja

Zagreb, 2014

SVEUČILIŠTE U ZAGREBU
FAKULTET STROJARSTVA I BRODOGRADNJE
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Povjerenstvo za završne ispite studija strojarstva za smjerove:
procesno-energetski, konstrukcijski, brodostrojarski i inženjersko modeliranje i računalne simulacije

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ZAVRŠNI ZADATAK

Student: **Davor Stjelja** Mat. br.: 0035181612

Naslov rada na hrvatskom jeziku: **Mjerenje toplinske provodnosti kapljevina**

Naslov rada na engleskom jeziku: **Measurement of heat conductivity of liquids**

Opis zadatka:

Potrebno je opisati metodu za mjerenje toplinske provodnosti kapljevina koja se bazira na usporedbi samozagrijanja platinskog otporničkog termometra u kapljevini poznate toplinske provodnosti i njegovog samozagrijanja u kapljevini čiju toplinsku provodnost želimo odrediti.

U radu je potrebno izraditi:

- Pregled teorijskih podloga za mjerenje toplinske provodnosti kapljevina.
- Opis metode bazirane na usporedbi samozagrijanja platinskog otporničkog termometara u dvjema kapljevinama sa potrebnim teorijskim podlogama i formulama.
- Shematski prikaz mjernog sustava sa kontrolnim i pomoćnim uređajima.
- Opis postupka ispitivanja.
- Opis glavnih sastavnica mjerne nesigurnosti sa procjenom mjerne nesigurnosti ispitivanja.
- Tablični i grafički prikaz rezultata ispitivanja.

U radu navesti korištenu literaturu i eventualno dobivenu pomoć.

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Prof. dr. sc. Igor Balen

I hereby declare that this thesis is entirely the result of my own work and knowledge obtained during my studies, except where otherwise indicated. I have fully cited all used sources and I have only used the ones given in the list of references.

I would like to begin expressing my gratitude to my supervisor, Professor Davor Zvizdić who made my work at MIKES and this thesis possible.

I am grateful to Dr. Martti Heinonen who was my supervisor at The centre for metrology and accreditation (MIKES) in Espoo, Finland. Without his attentive guidance, endless patience and encouragement through my work at the MIKES and after, this thesis would not have been possible to accomplish.

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Davor Stjelja, February 25th, 2014

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NOMENCLATURE

Roman	Unit	Description
A	m^2	surface area
a	m^2/s	thermal diffusivity
c	J/(kg K)	specific heat capacity
C	-	constant for calculating sensitivity coefficient of electric current
c	-	constant for standard uncertainty of difference in conductivity between two liquids
c_m	-	constant for standard uncertainty of maximum difference in conductivity between two liquids
I	A	electric current
I_{1C}	A	lower electric current
I_{2C}	A	higher electric current
ΔI_{max}	A	standard deviation at highest current
L	m	length
Q	J	heat
$\vec{q}$	W/m^2	heat flux density
q	W/m^2	magnitude of heat transmission
r	m	radius
R	Ω	electric resistance
R_0	Ω	electric resistance at 0°C
t	s	time
t	°C	temperature
t_{M1C}	°C	temperature of measurand liquid at higher current
t_{M2C}	°C	temperature of measurand liquid at lower current
t_{R1C}	°C	temperature of reference liquid at higher current

t_{R2C}	°C	temperature of reference liquid at lower current
T	K	temperature
ΔT	K	temperature difference
ΔT_M	K	temperature difference of measurand liquid between currents
ΔT_R	K	temperature difference of reference liquid between currents
ΔT_{SH}	K	self-heat error
$u(C)$	A	standard uncertainty of electric current
$u(c)$	W/(m K)	standard uncertainty of constant for determining difference in conductivity between two liquids
$u(res)$	m	standard uncertainty of resolution
$u(\Delta\lambda)$	W/(m K)	standard uncertainty of difference in conductivity between two liquids

Greek	Unit	Description
ϑ	°C	temperature
λ	W/(m K)	thermal conductivity
λ_G	W/(m K)	thermal conductivity of glass tube
λ_L	W/(m K)	thermal conductivity of liquid inside the tube
λ_M	W/(m K)	thermal conductivity of measurand liquid
λ_R	W/(m K)	thermal conductivity of reference liquid
λ_X	W/(m K)	reference thermal cond. of tap water
λ_{XM1}	W/(m K)	measured thermal cond. of tap water compared to distilled water
λ_{XM2}	W/(m K)	measured thermal cond. of tap water compared to ethylene glycol
ρ	kg/m^3	density
Φ	W	heat flux
Φ_M	W	heat flux in measurand liquid
Φ_R	W	heat flux in reference liquid
$\Delta\Phi_E$	W	difference of electric power between two currents
$\Delta\Phi_{thermal}$	W	difference of heat flux between two currents
ω	rad/s	angular frequency

SAŽETAK

U sklopu ovoga rada osmišljena je i napravljena je mjerna linija za mjerenje toplinske provodnosti kapljevina u laboratorijima mjeriteljskog instituta MIKES u gradu Espoo, Finska. Svrha rada je objasniti teorijske osnove potrebne za mjerenje toplinske provodnosti kapljevina, te napraviti mjernu metodu koja koristi postojeću opremu toplinskih laboratorija bez dodatnih investicija. Za mjerenje toplinske provodnosti koristi se efekt samozagrijavanja platinskog otporničkog termometra (PRT), te se za određivanje toplinske provodnosti uspoređuju izmjerene temperature mjerene kapljevine sa temperaturama referentne kapljevine. Nakon što je osmišljena mjerna linija, uspoređivanjem kapljevina poznatih svojstava ustvrdili smo njezinu valjanost.

Ključne riječi: toplinska provodnost, kapljevine, PRT, samozagrijavanje, mjeriteljstvo

SUMMARY

The concept of this paper was to develop a method for measuring the thermal conductivity of liquids, which was done in the laboratories of Centre for metrology and accreditation (MIKES) in the city of Espoo, Finland. The purpose of this work was to explain the theoretical bases required for measuring the thermal conductivity of liquids and to develop a method which can be applied in temperature laboratories from the existing equipment without further investment. This method uses the self-heating effect of a platinum resistance thermometer (PRT), and compares the measured temperatures from the measurand liquid to the reference liquid to determine the thermal conductivity of the measurand liquid. Once that the measurement method has been developed, a validation was made by comparing liquids of known thermal properties.

Keywords: thermal conductivity, liquids, PRT, self-heating, metrology

1. INTRODUCTION

Thermal conductivity values are necessary whenever a heat transfer problem is to be evaluated. There are many methods for measuring the thermal conductivity of water but all of them require purchasing or building new equipment. The purpose of this work is to develop and verify a new method, which can be used with the existing equipment in temperature laboratories.

First, I will describe the theoretical basis required for the development of this method: heat transfer, thermal conduction, existing methods for measuring thermal conductivity, platinum resistance thermometers and measurement of resistance, self-heating of PRTs. Afterwards, I will describe the developed method, with a mathematical model, a numerical simulation, a measurement setup and procedure, the verification of method and measurement uncertainty.

1.1. Thermal conduction

Heat always flows from a higher temperature field to a lower temperature field. In nature there are three mechanisms of heat transfer; it can be transferred together with all the mechanisms, with only two of them or with only one mechanism. Those three mechanisms are:

- Conduction
- Convection
- Thermal Radiation

Convection is the transfer of heat from one place to another by the movement of fluids. Thermal Radiation is electromagnetic radiation generated by the thermal motion of charged particles in matter.

Thermal conduction is the transfer of heat in solids, liquids, gases and plasmas where temperature gradient exists, which generates collisions of particles and microscopic diffusion. Conduction only takes place within a material (object) or between two objects in contact (directly or indirectly). In solids, conduction is a result of vibration and collision between molecules, free electrons and phonons. On the other hand, in liquids and gases, conduction is a result of collisions and diffusions of molecules during their random motion. Conduction is greater in solids because of their dense structure, which enables atoms to transfer energy by vibration. Internal energy diffuses as rapidly moving or vibrating atoms and molecules interact with their neighboring particles, transferring some of their kinetic and potential energy.

Fluids are typically less conductive then solids, as they have larger distances between molecules and atoms.

Thermal contact conductance refers to a drop in conductivity between two solids in contact, even though they are made from the same material.

In metals there is a connection between thermal and electrical conductivity, as they usually have the same ratio, following the Wiedemann-Franz law. The reason for this is in the metallic bond, which has in its structure free-moving electrons which are able to transfer heat rapidly. Free-moving electrons are also the reason for conducting electric current and therefore there is a relationship between thermal and electrical conductivity in metals.

1.2.Thermal conductivity

In the world of engineering there is a need to quantify how good or bad materials are at conducting heat. For example, let's take a classical shell and a tube heat exchanger, where we have a liquid of higher temperature inside the tube and on the outside is a liquid of lower temperature. To calculate the parameters necessary for designing the heat exchanger, we need to know how well heat transfers from one fluid to another and one of the most important properties is thermal conductivity. We have to take into account the thermal conductivity of both liquids, conductivity of pipes made of steel and also conductivity of steel shell, insulation material and air outside of the exchanger (even though the last one can be neglected).

1.2.1. Fourier's law

Mathematically, thermal conductivity is described by Fourier's law, which states that time rate of heat transfer through a material is proportional to the negative gradient of temperature and to the area through which heat is flowing.

Fourier's law can be written in two forms:

1.2.1.1. Differential form

Where we look at flow rates or fluxes locally

$$\vec{q} = -\lambda \nabla T \tag{1.1}$$

The equation (1.1) states that local heat flux density $\vec{q}$ is equal to product of thermal conductivity λ and negative local temperature gradient ∇T.

1.2.1.2. Integral form

In which we look at the amount of energy flowing into and out of a body
By integrating the differential form over the material's total surface *S*, we obtain the integral form of Fourier's law.

$$\frac{\partial Q}{\partial t} = -\lambda \oint_S \vec{\nabla} T \cdot \overrightarrow{dA} \tag{1.2}$$

Where $\frac{\partial Q}{\partial t}$ is amount of heat transferred in unit of time (W) and $\overrightarrow{dA}$ is surface area element (m^2)

1.2.2. Thermal conductivity units

In SI units, thermal conductivity is measured in watts per meter kelvin (W/(m K)). This unit shows that, in a material, one joule of energy per one second (that is one watt) moves through the distance of one meter due to a temperature difference of one kelvin. The imperial system measures in the British thermal unit per hour (which is power) per foot per Fahrenheit degree (Btu/(hr·ft·°F). In HVAC engineering and textile industry unit (clo) (which express thermal resistance of a material) is also used for thermal comfort applications.

1.2.3. Influencing factors

- Temperature – materials change their thermal conductivity with temperature change, pure metal's conductivity decreases with the rise of temperature, while it is the opposite case with water.
- Material phase – Each material's phase has a different thermal conductivity (ice= 2.18 W/(m K), water= 0.56 W/(m K) at 0°C)
- Material structure- pure crystalline substances can exhibit different thermal conductivities along different axes. Sapphire in one axis has t. conductivity of 32 and in other of 35 W/(m K).
- Magnetic field – Righi-Leduc effect describes the changes in thermal conductivity when placing a conductor into a magnetic field.

1.3.Measuring thermal conductivity of liquids

The measurement of thermal conductivity of liquids is always a challenging task.

From Fourier's law, it can be seen that, if we know steady-state one dimensional heat flux and measure temperature from two locations and from its difference, thermal conductivity can be calculated.

$$\lambda = \frac{q / A}{\Delta T / L} \tag{1.3}$$

Where q is magnitude of heat transmission, ΔT is temperature difference across length L and cross-sectional area A.

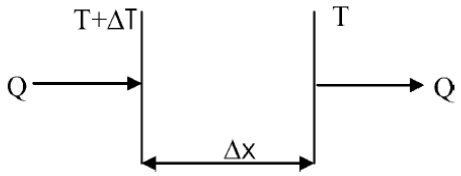

Figure 1. Principle of heat conduction

In practice, there are a few problems. First of all, a one-dimensional temperature field is difficult to achieve, even in homogenous solids. Secondly, with liquids, which is the topic of this work, there is the ever-present convection current. Convection would increase heat transfer and have an effect on the measured temperature difference, which would in the end, give a wrong value for thermal conductivity. In all thermal conductivity measurements convection should be suppressed. To minimize its effect we should avoid temperature gradients in vertical directions (gravity), or if its needed, it is better to put the heater on top of a liquid than on the bottom, because of the buoyancy. Likewise, we should avoid larger temperature differences in the field and do the measurement as fast as possible. Even though convection is ever-present in fluids during the heat transfer, by proper design of the method it can be neglected.

In all of the existing methods the main focus was on minimizing the effect of convection.

1.4.Comparison of methods

The methods for measuring thermal conductivity of liquids can be separated into three parts:

- Steady state methods (coaxial cylinders or parallel plates)
- Transient state methods (Hot wire, flat plate stepwise heating method and 3ω method)
- Laser flash method

1.4.1. Steady state methods

- Difficult to avoid the effect of convection
- Longer period of measuring time

1.4.1.1. Parallel plate method

A small amount of fluid is placed between two parallel round pure copper plates. As the total heat supplied by the main heat flows between the upper and lower plate, the thermal conductivity of the liquid can be calculated from Fourier's law. To assure that there is no heat loss between the liquid and its surroundings, guard heaters are used to maintain a constant temperature of liquid.

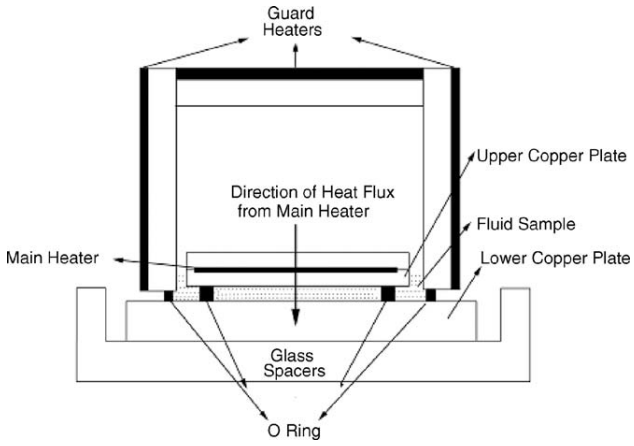

Figure 2. Experimental set up for steady-state parallel-plate method

1.4.1.2. Coaxial cylinders method

A liquid is placed in the space between the two concentric cylinders. The inner cylinder is made from copper and in the inside electrical heater is placed. The outer cylinder is made from galvanized material and the back and the front side of the equipment are insulated to nullify the heat loss during the measurement. Two thermocouples are used to measure the outside surface temperature of cylinders. The required measurements for thermal conductivity are the temperatures from both thermocouples, the voltage and the current of the heater.

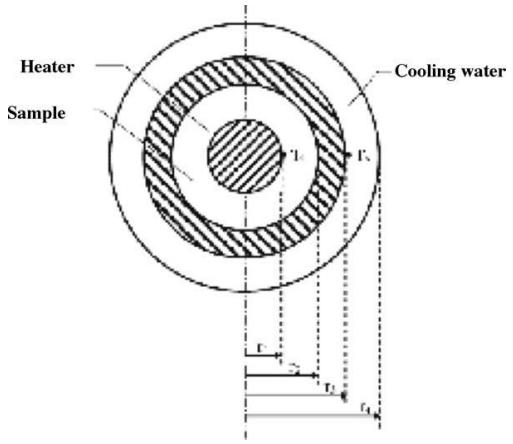

Figure 3. Coaxial cylinders method

1.4.2. Transient state methods

1.4.2.1. Hot wire method

The hot wire method uses the temperature response of liquid to determine its thermal conductivity. The heat source is a thin platinum wire which is subjected to an abrupt electrical pulse. The temperature of the wire rises and is measured by the same wire which is used as a thermometer. The temperature rise is measured during a short period of time and depends on t. cond. of liquid.

The thin platinum wire is used as a heater and a sensor in the closed cylinder, thermal conductivity is defined from the temperature rise in wire. For electrically conductive liquids a mercury filled glass capillary is used.

- Very short time of measurement (typically up to 1 second)
- Amount of liquid is usually not small
- Convection is liable to appear, although measurements are short, it's hard to determine when convection starts to appear

The typical diameter of cylinder is around 20mm and wire 0,5mm, the temperature difference is around 4K

1.4.2.2. Flat plate stepwise method

The flat plate above the sample liquid is heated step by step with electric current and the thermal conductivity of liquid is determined from the liquid temperature rise

- Temperature distribution in the sample fluid is uniform, because of the small liquid sample
- Convection is unlikely to appear, measurement time is very short
- Method is not suitable for measuring high electrically conductive fluids

1.4.2.3. 3ω method

In 3ω method, a metal strip is used as a heater and as a thermometer. This method is relatively fast and heats a small volume of liquid, so small samples can be used (in literature I have found a thermal conductivity measurement of 12 nl liquid). Also, short measurement time helps to minimize convection and radiation.

Theory of 3-omega method is more complicated to understand, but can be explained in a few words: When an alternating current (AC) is used to excite the heater at a frequency 1ω which makes the temperature of the strip to oscillate at 2ω due to Joule heating, this leads to third harmonic (3ω) in the voltage signal. By monitoring 3ω component of the voltage, $V_{3\omega}$, over the heater, the temperature oscillation can be measured, from which thermal conductivity can be calculated.

I have been researching and developing this method with MIKES and currently, the thermal conductivity of water drop has been successfully measured. The heater size used was 50 μm wide and 3 mm long with dielectric layer made from Al_2O_3 which is 135 nm thick.

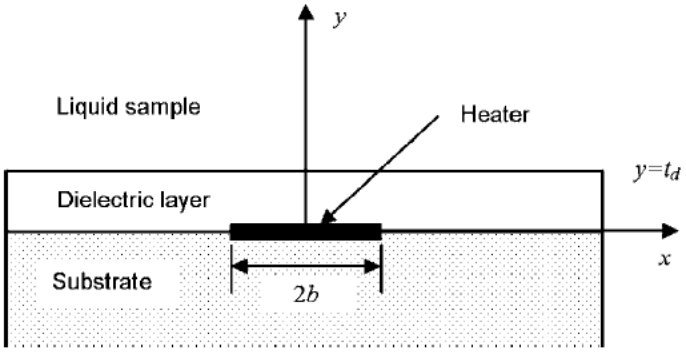

Figure 4. Schematic diagram of the 3 – ω technique for measuring the thermal properties of liquids.

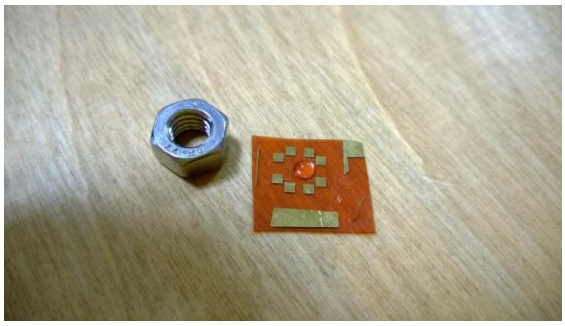

Figure 5. Amount of liquid required to measure its properties using 3-ω technique in MIKES

1.4.3. Laser flash method

A laser beam is used as a heat source of very short duration. The sample liquid is pressed between metal disk, which receives the laser beam energy, and a sample holder. The thermal conductivity is measured from the temperature fall of the front surface of the metal disk and the measurement of the heat discharge into the liquid layer.

- This method can be applied to liquids of high electrical conductivity
- Desirable method for liquids at higher temperatures
- Convective heat transport is minimized

1.5.Platinum resistance thermometers (PRTs)

A platinum resistance thermometer is a device that determines the temperature by measuring electrical resistance of the platinum wire and temperature can be calculated from calibration data.

Many metals have the property of and approximate linear rise in resistance with temperature, which makes them useful as temperature sensors. Platinum sensors are the most reproducible, because platinum is a stable and unreactive metal which can be easily drawn in thin wires and is not too soft.

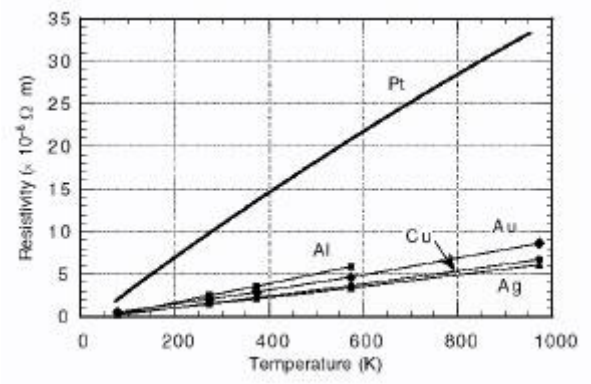

Figure 6. The resistivity of five metallic elements plotted on a linear scale as a function of temperature

PRTs are usually made in Pt100 form, which means that the platinum wire was made in a way that at 0°C platinum wire resistance is 100 Ω. Every additional degree Celsius gives approximately a 0.4 Ω rise. If we use the typical measuring current of 1 mA at 0°C we will have a voltage drop of 100 mV and this would change approximately by 0.4 mV with every additional Celsius.

For the highest accuracy Standard Platinum Resistance Thermometers are used, they are specially glass shielded PRTs, usually made in Pt25 version (at 0°C their resistance is 25 Ω) and calibrated at fixed points of the International temperature scale 1990 (ITS-90).

1.5.1. Calibration

To determine the linearity of the relationship between absolute temperature and resistance SPRTs and PRTs need to be calibrated at different temperatures. Two types of calibration exist:

- Fixed point calibration
  - Most accurate method used mostly for SPRTs as it reproduces actual conditions of ITS-90
  - Thermometers are compared to triple points, freezing points, boiling points or melting points of water, zinc, argon, tin, etc. to generate known and repeatable temperature
- Comparison calibration
  - thermometers that are to be calibrated are immersed in baths whose temperature is uniformly stable (mostly water, silicon oil, ethanol, methanol, etc.) and their readout is compared to already calibrated thermometers.

- this method is less accurate but is cheaper and faster as it can be automated and more probes can be calibrated at the same time.

1.5.2. Construction of PRTs

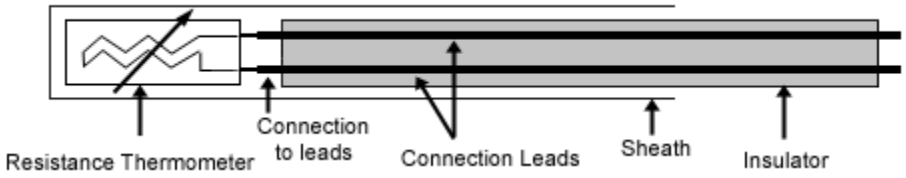

Figure 7. Construction of PRT

In reality, platinum resistance thermometers are not just platinum wires, they are connected with connection leads (usually made from copper) which are insulated with electric insulator. For the thermometer to be protected from chemical reactions in measuring liquid and to have some mechanical resistance a housing or a sheath is used, made mostly from some chemically inert metal alloy.

1.5.3. Wiring configurations

As it was explained before, the actual measurements with PRTs are resistance measurements, so a knowledge of different ways of resistance measurement is necesary.

1.5.3.1. Two-wire configuration

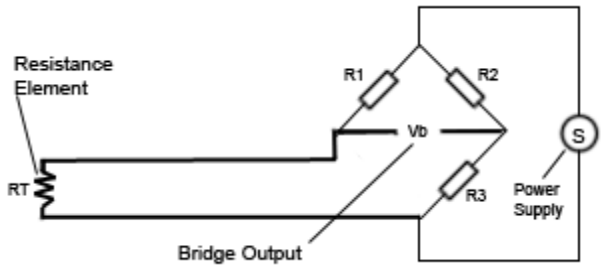

Figure 8. Two-wire configuration

They are used for simple, low accuracy measurements as the resistance of the wire connecting the sensor to the bridge is counted into the result.

1.5.3.2. Three-wire configuration

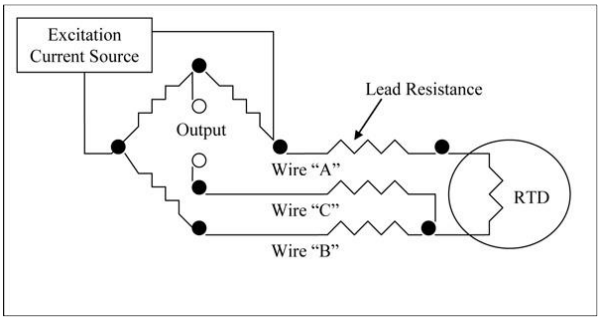

Figure 9. Three-wire configuration

The three-wire configuration is most often used in the industry.

To cancel-out wire resistance, wire A and B need to be of similar length [Figure 9.].

1.5.3.3. Four-wire configuration

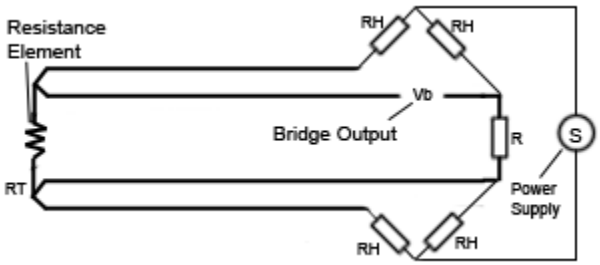

Figure 10. Four-wire configuration

The four-wire configuration is even more accurate than the three-wire because it is able to compensate completely for the resistance of the wires without having to pay particular attention to the length of each wire.

This configuration was used in making measurements for this thesis.

1.5.4. Self-heating of PRTs

The self-heating effect is a well-known phenomenon in resistance thermometers. For measuring resistance, electric current flow through the sensor is necessary, as it, in addition to current, also dissipates power and additionally heats up the PRT. To minimize this effect, it is necessary to introduce the self-heat error into calculation. The self-heat error can be calculated by measuring the temperature with various measurement currents and using this formula:

$$\Delta T_{SH1} = (T_2 - T_1)\left[\frac{I_1^{\,2}}{I_2^{\,2} - I_1^{\,2}}\right] \tag{1.4}$$

Where ΔT_{SH1} is self-heat error at I_1, T_1 and T_2 temperatures at currents I_1 and I_2. The result is then subtracted from the measured temperature. This procedure is only suitable in cases when temperature stability is good, such as very stable baths or fixed points. Equation is accurate to better than 1% for 100 Ω Platinum resistance thermometers, for self-heating changes up to 1°C.

2. COMPARATIVE SELF-HEATING METHOD FOR MEASURING THE THERMAL CONDUCTIVITY OF LIQUIDS

It was necessary to measure the thermal conductivity of liquids with a method that can be applied in NMIs (national metrology laboratories) or similar temperature laboratories, without any new investment for equipment. The basic model for this method has been developed and my task for this thesis was to validate and improve it.

The main idea of this method was to use self-heating of the platinum resistance thermometer to produce heat which is dissipated through the surrounding liquid and to measure the liquid's temperature. By comparing the temperature rise between two liquids, one of unknown conductivity and the other reference liquid which has well-known thermal conductivity, the thermal conductivity of measured liquid could be calculated.

2.1. Assumptions

In the mathematical model we made a few assumptions, in order to either simplify the calculation (e.g. heat flows only radially) or make this model possible (convection and radiation is neglected).

2.1.1. Convection

Convection is known as a major problem in the measurements of the thermal conductivity of liquids. Every method's goal is to achieve this. In this method we have done two things to minimize effect of convection. Firstly, temperature differences between the PRT sensor and outer surface of glass tube are very small (maximum difference is less than 0.2°C) and convection is dependent on temperature gradient. Secondly, most of the heat flow goes in a radial direction and PRT is placed horizontally, to avoid the effect of gravity. Later on, we have modeled a setup in Ansys Mechanical module as well as experimented with different convection settings and the resulting effect was negligible.

Also, I need to emphasize that this is a comparative model between two liquids, which means that even the small effect of liquid's convection is canceled out by other liquid. Certainly different liquids have a different potential for convection but all that was said points to it being negligible. While doing measurements we have found more significant problems than the convection effect, if it even exists.

2.1.2. Radiation

Radiation can be neglected because temperatures in this work are low and the medium is liquid, also, different radiation models were tested in our numerical simulation and there wasn't any change in temperature.

2.1.3. One-dimensional heat flow

To simplify the mathematical model, we assume that heat flows only in one dimension; that is radially. Most of the heat flow going in other directions will cancel-out when comparing results from reference liquid to measured liquid. Later on, we will see that the vertical heat flow is the main problem of this method and how to deal with it.

2.1.4. Steady-state model

During the measurements it was always necessary to wait until the system stabilized and after enough time had passed the model could be presumed to be in steady-state and any potential uncertainty was included in the uncertainty budget.

2.2.Mathematical expression of the model

To calculate the thermal conductivity of liquid using this model we needed the knowledge of conductive heat transfer. The basic of conductive heat transfer is Fourier's law:

$$q = -\lambda \frac{\partial \vartheta}{\partial n} \tag{2.1}$$

Where λ is thermal conductivity $\left(\frac{W}{m \cdot K}\right)$,

$\frac{\partial \vartheta}{\partial n}$ is temperature gradient and q is local heat flux.

The shape of the PRT sensor is a cylinder, as well as the glass tube that surrounds the sensor, so we needed the equation for Fourier's law which satisfies the cylindrical coordinate system:

$$\frac{\partial \vartheta}{\partial t} = a\left(\frac{\partial^2 \vartheta}{\partial r^2} + \frac{1}{r}\frac{\partial \vartheta}{\partial r} + \frac{1}{r^2}\frac{\partial^2 \vartheta}{\partial \varphi^2} + \frac{\partial^2 \vartheta}{\partial z^2}\right) \pm \frac{\Phi_v}{\rho c} \tag{2.2}$$

If we assumed that the heat flow goes only in the direction of the cylinder's radius and introduce boundary conditions we got the equation for conductive heat flow in one cylinder.

$$\Phi = \frac{t_1 - t_2}{\frac{1}{2\pi L\lambda} ln \frac{r_2}{r_1}} \quad (2.3)$$

Where t_1 and t_2 are temperatures at radius r_1 and r_2 and L length of cylinder.

In this case we had two concentric cylinders (PRT and glass tube) so the necessary equation was

$$\Phi = \frac{2\pi L(t_1 - t_3)}{\frac{1}{\lambda_L} ln \frac{r_2}{r_1} + \frac{1}{\lambda_G} ln \frac{r_3}{r_2}} \quad (2.4)$$

λ_L –thermal conductivity of liquid inside of tube

λ_G – thermal conductivity of borosilicate glass tube

t_1 –temperature measured with PRT

t_3 –temperature of outer surface of tube, we assume it is the same as bath temperature

r_1 – radius of PRT

r_2 – inner radius of tube

r_3 – outer radius of tube

L – length of cylinder

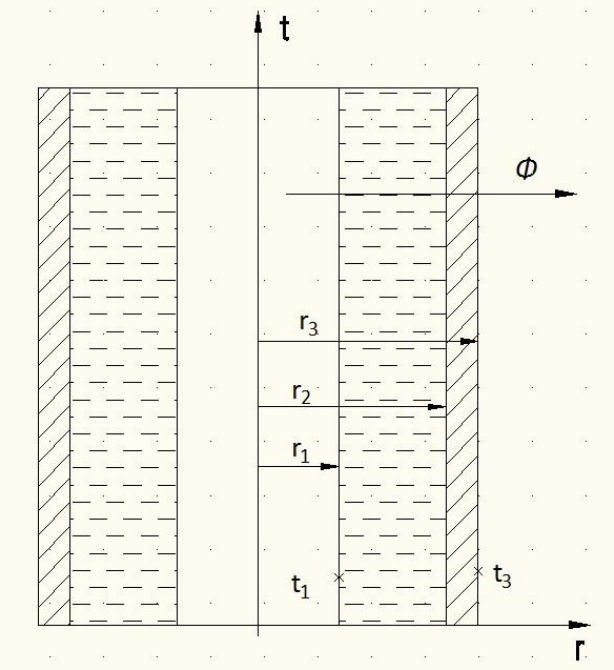

Figure 11. 2D model for conductive heat transfer

This method was based on comparing the heat flow differences at two individual currents between the reference liquid and other(measured) liquid.

$$\Phi_{R1C} = \frac{2\pi L(t_{R1C} - t_3)}{\frac{1}{\lambda_R} ln\frac{r_2}{r_1} + \frac{1}{\lambda_G} ln\frac{r_3}{r_2}} \tag{2.5}$$

$$\Phi_{R2C} = \frac{2\pi L(t_{R2C} - t_3)}{\frac{1}{\lambda_R} ln\frac{r_2}{r_1} + \frac{1}{\lambda_G} ln\frac{r_3}{r_2}} \tag{2.6}$$

Where:

Φ_{R1C} - heat flow at higher current in reference liquid [W]

Φ_{R2C} - heat flow at lower current in reference liquid [W]

t_{R1C} - measured temperature at higher current [°C]

t_{R2C} - measured temperature at lower current [°C]

λ_R - thermal conductivity of reference liquid [W/(m K)]

By subtracting one heat flow from another, we got the difference in heat flow for reference liquid

$$\Phi_{R1C} - \Phi_{R2C} = \frac{2\pi L(t_{R1C} - t_{R2C})}{\frac{1}{\lambda_R} ln\frac{r_2}{r_1} + \frac{1}{\lambda_G} ln\frac{r_3}{r_2}} \tag{2.7}$$

Applying the same procedure for measured liquid provided us the heat flow difference

$$\Phi_{M1C} - \Phi_{M2C} = \frac{2\pi L(t_{M1C} - t_{M2C})}{\frac{1}{\lambda_M} ln\frac{r_2}{r_1} + \frac{1}{\lambda_G} ln\frac{r_3}{r_2}} \tag{2.8}$$

We took the assumption that heat dissipated from the sensor goes only in radial direction and that heat flow can be calculated from Joule's first law:

$$\Phi = I^2 R \tag{2.9}$$

Where:

I - electric current used in measurement of sensor's resistance

R - electric resistance of sensor at current temperature

And in this case it gave us

$$\Phi_{M1C} - \Phi_{M2C} = {I_{1C}}^2 R - {I_{2C}}^2 R = \Phi_{R1C} - \Phi_{R2C} \tag{2.10}$$

If heat flow only depends on current and resistance of PRT, it will be the same no matter which liquid is surrounding PRT sensor, which gives us:

$$\frac{(t_{R1C} - t_{R2C})}{\frac{1}{\lambda_R} ln\frac{r_2}{r_1} + \frac{1}{\lambda_G} ln\frac{r_3}{r_2}} = \frac{(t_{M1C} - t_{M2C})}{\frac{1}{\lambda_M} ln\frac{r_2}{r_1} + \frac{1}{\lambda_G} ln\frac{r_3}{r_2}} \tag{2.11}$$

From which we could calculate the thermal conductivity of measured liquid

$$\lambda_M = \frac{ln\frac{r_2}{r_1}}{\frac{t_{M1C} - t_{M2C}}{t_{R1C} - t_{R2C}}\left(\frac{1}{\lambda_R} ln\frac{r_2}{r_1} + \frac{1}{\lambda_G} ln\frac{r_3}{r_2}\right) - \frac{1}{\lambda_G} ln\frac{r_3}{r_2}} \tag{2.12}$$

2.3.Numerical simulation of the model

After we did the first measurements, the results were not satisfying. So we started to develop a 3D model and a numerical simulation of the measurement setup to analyze sources of the problems more accurately, since we could quickly make certain changes and immediately see how they affect temperature field around the sensor.

2.3.1. 3D model

I used Solidworks 2012 software to create a 3D model of the PRT with a tube and a measurement (or a reference) the liquid which is immersed into the water bath. The dimensions of the glass tube and the PRT were measured with a digital caliper device (included in the uncertainty budget). My 3D model was composed of a PRT sensor, which is further divided into two parts, the upper part of the PRT and the sensor part (tip of PRT), the glass tube, the liquid inside of tube and the bath liquid around glass tube. The reason for dividing the PRT into two parts was to simplify the simulation. The liquid was also made in Solidworks and there were certain problems with the simulation, so the liquid was modeled to follow the curvature of PRT and the glass tube. After every part was created in Solidworks module assembly, parts were assembled into one model. [Figure 12.] shows how was liquid created in Solidworks to satisfy simulation conditions. Highest part on the figure shows shape of liquid, middle part is PRT and lowest is glass tube. Liquid follows curvature of tube's and PRT's shape. [Figure 13.] shows the assembled model of the measuring setup consisting of: the water bath liquid in which the liquid filled glass tube with the PRT was immersed

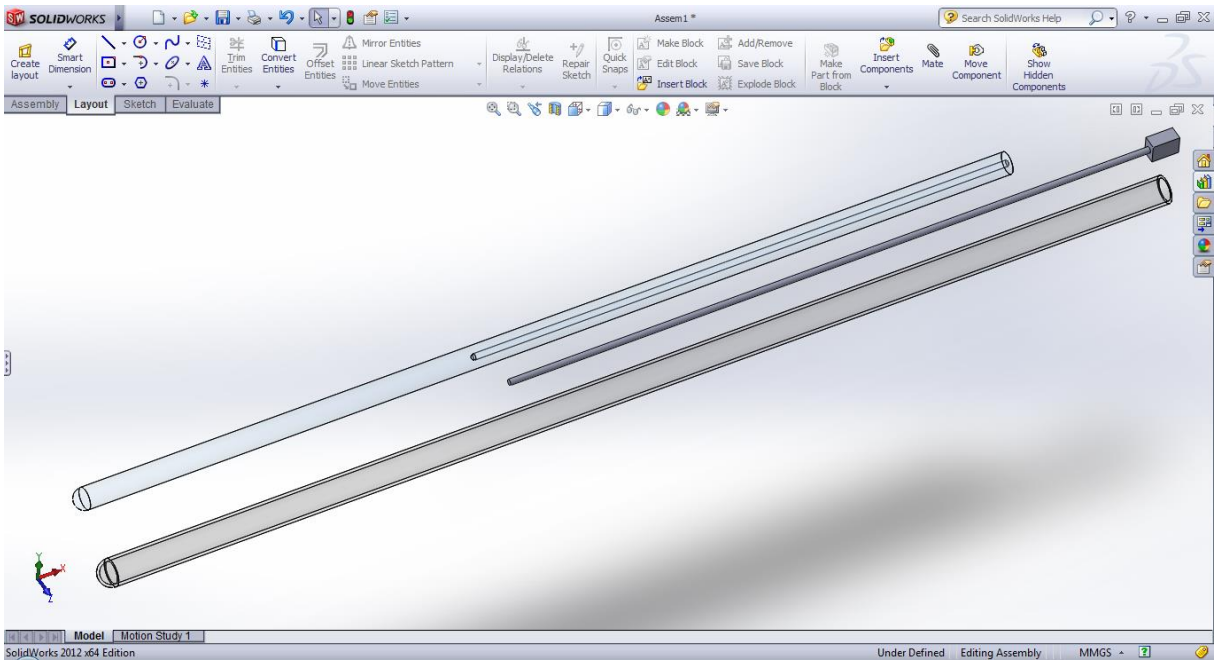

Figure 12. 3D parts made in Solidworks

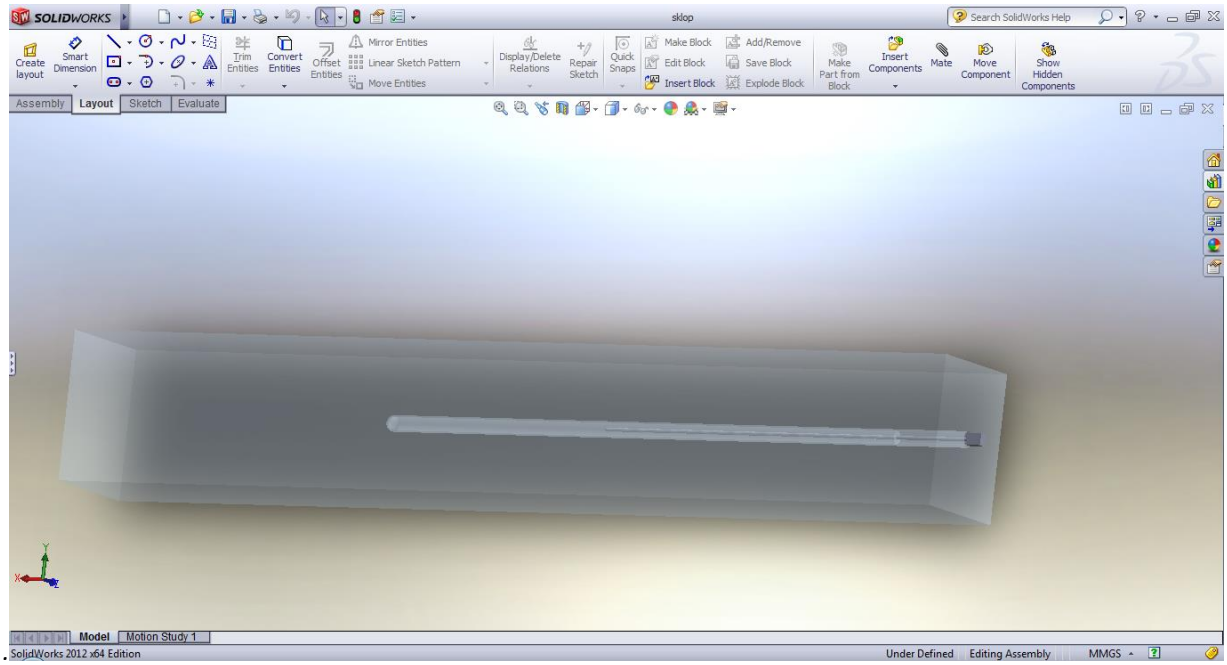

Figure 13. 3D assembled parts in Solidworks

2.3.2. *Numerical simulation*

The numerical simulation was made in Ansys software and its module in Ansys Mechanical and steady-state thermal system. The 3D model that was made in Solidworks software and imported

into Ansys. Before generating the mesh, in Engineering Data in Ansys, materials were chosen and were assigned, along with their properties, to the matching part. This case is simple as its geometry, the default mesh setup was used.

The simulation setup consisted of: the initial temperature of the system, the water bath temperature and the internal heat generation of the PRT sensor. The initial temperature of the whole system was set at the average measured bath temperature. Internal heat generation is dissipated power divided by sensor's volume (W/m^3), power was assumed from resistance of PRT at that temperature and from current used in measurement $P=I^2R$ and result was divided by volume of sensor. After solving we could see the temperature on the sensor or temperature distribution through liquid, but because of small temperature differences we decided to monitor only the temperature of the sensor.

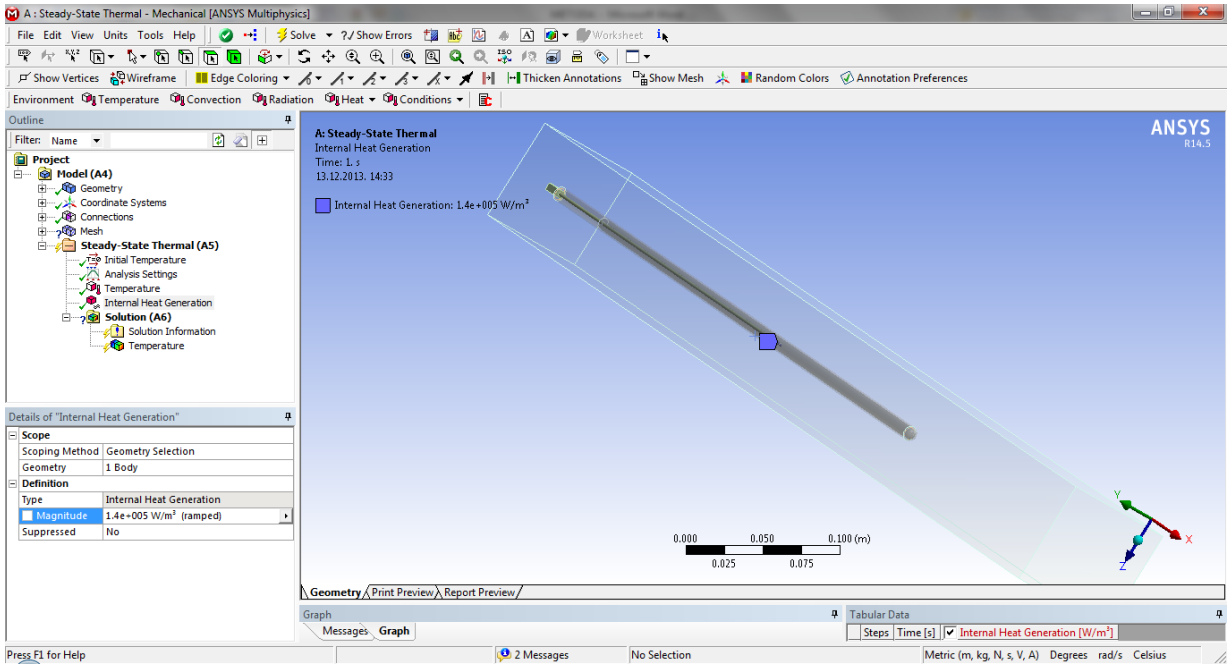

Figure 14. Ansys Mechanical module showing Internal Heat Generation setting

2.3.3. Comparison of simulation and reality

The simulation cannot be used in the same way as the measurement. In the simulation, thermal conductivity is material property which is included before the simulation and in the measurement we want to find the thermal conductivity. A direct comparison between the simulation and the measurement is not possible. To make a simulation close to the real world would be really difficult, but the temperatures in the simulation are not far from reality (less than 0.1°C).

Even so, the simulation proved to be a good tool when wanting to see how much changing one parameter would affect final results, for example: heating and measuring the temperature of the liquid with different thermal conductivity. The simulation helped to discover different heat flow in the vertical direction in different liquids which will later be explained.

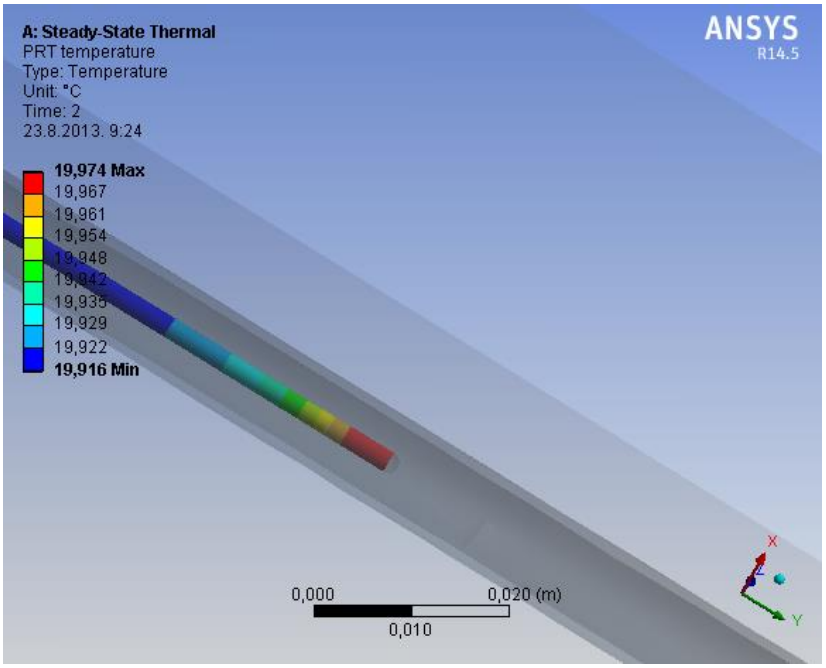

Figure 15. Example of simulated heat flow with resulting temperature field over PRT

2.4.Partial self-heat error and calibration

All PRT sensors that have been used in these measurements had already been officially calibrated by MIKES. They were compared to the reference PRTs which were compared to SPRTs and SPRTs were calibrated by taking into account their self-heating effect. This means that the PRTs used in this project had already taken into account self-heating at 1 mA measurement current. For this method we needed to use not only 1 mA current but also higher currents (e.g. $\sqrt{2}$ or 5 mA) and their partial self-heat error needed to be measured. In this case self-heating could not be neglected completely, because the self-heat effect was used to heat the liquid sample. So the idea was to cancel out the self-heat effect due to thermal resistance in the PRT sensor and coating but leave the effect that self-heating has on surrounding liquid. It was decided to call it the partial self-heat error. The partial self-heat error was measured by the PRT by immersing it in the bath and measuring its temperature on different currents (from 1 mA to 5 mA). It was assumed that temperature rise was only present because of the thermal resistance in the sensor and in PRT's

coating. Heat flow that was transmitted around the PRT was neglected because of the high temperature stability of the bath and the high convection of circulating water, assuming partial self-heat would not have an effect on its temperature rise.

The collected electric resistance data from measurement was analyzed in the following way. Average measured resistance at higher current ($\sqrt{2}$ or 5 mA) was subtracted from 1 mA averaged resistance. This rise in resistance by self-heating was deducted from the measurements of thermal conductivity in the glass tube and by applying coefficients from calibration, temperatures were calculated, which were used in finding the thermal conductivity of liquid.

Table 1. Measured self-heat error in water bath at 20°C

SAB				Check
20°C water	1 mA	Sqrt(2) mA	5 mA	1 mA
Resistance	107.7772383	107.7800272	107.8423401	107.777306
Temp	19.95542	19.96259	20.12298	19.95559
Burns1&2	19.9140425			
Self-heat error		0.00279	0.06510	

Table 2. Measured self-heat error in water bath at 50°C

SAB				Check
50°C water	1 mA	Sqrt(2) mA	5 mA	1 mA
Resistance	119.3760413	119.3789747	119.4444435	119.376066
Temp	49.94219	49.94981	50.11984	49.94226
Burns1&2	49.896895			
Self-heat error		0.00293	0.06840	

Table 3. Measured self-heat error in water bath at 80°C

SAB				Check
80°C water	1 mA	Sqrt(2) mA	5 mA	1 mA
Resistance	130.8669227	130.8699877	130.938873	130.8670348
Temp	79.91833	79.92636	80.10688	79.91862
Burns1&2	79.8788675			
Self-heat error		0.00306	0.07195	

The influence of a different liquid in contact with the PRT was also tested. We used an ethanol bath and, in most cases, the partial self-heat error slightly increased compared to the water bath (average 4%). However, a different bath was used in this process, with lower stability and the result was a higher fluctuation of temperature. When we included the new partial self-heat error

into our thermal conductivity calculations for ethanol, the end results did not change substantially. Finally, it was decided that the difference in the partial self-heat error between ethanol and water was negligible.

Table 4. Measured self-heat error in ethanol bath at 20°C

SAB				Check
20°C ethanol	1 mA	Sqrt(2) mA	5 mA	1 mA
Resistance	107.8032465	107.80632	107.870975	107.8032311
Temp	20.02236	20.03026	20.19669	20.02232
Self-heat error		0.00307	0.06773	

3. MEASUREMENTS AND RESULTS

3.1. Measurement procedure and setup

As was previously explained, this method uses self-heating effect of PRT to heat the sample liquid located in the borosilicate glass tube which is immersed in a high precision water bath. For this method we used the equipment of Temperature laboratory in MIKES, Finland, which is listed here:

- Resistance bridge : ASL F700
- Water bath : Hart Scientific, High precision bath, 7037
- Reference resistors : Tinsley 100Ω
- Reference PRT :
  - 2x Burns Engineering 5614, Secondary reference PRT
  - 2x Fluke 5616, secondary reference PRT
- PRT sensor :
  - SAB MWT505- mineral insulated resistance thermometer
  - Pentronic Pt100 sensor
- Borosilicate glass tube
- LabVIEW application developed by MIKES

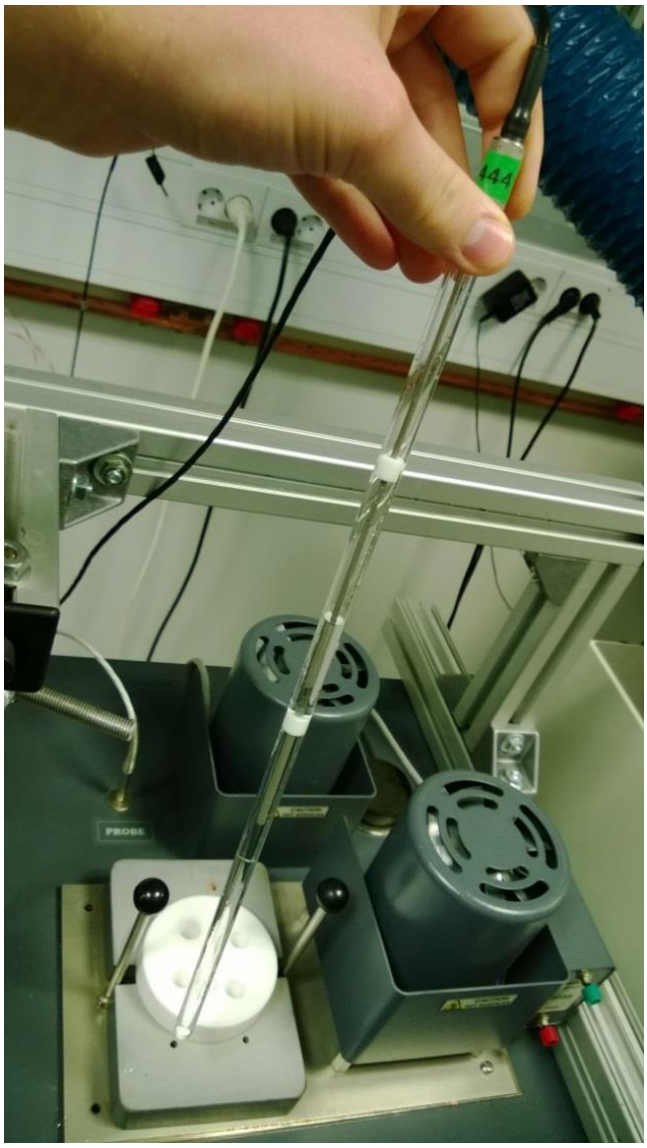

Figure 16. Measurement setup consisted of PRT with plastic distancers immersed in liquid inside glass tube

All equipment is calibrated by MIKES yearly, although, in this case, the correction for the PRTs is not needed (except for the reference PRTs for measuring the current temperature), because we are interested only in temperature differences not in absolute temp. values.

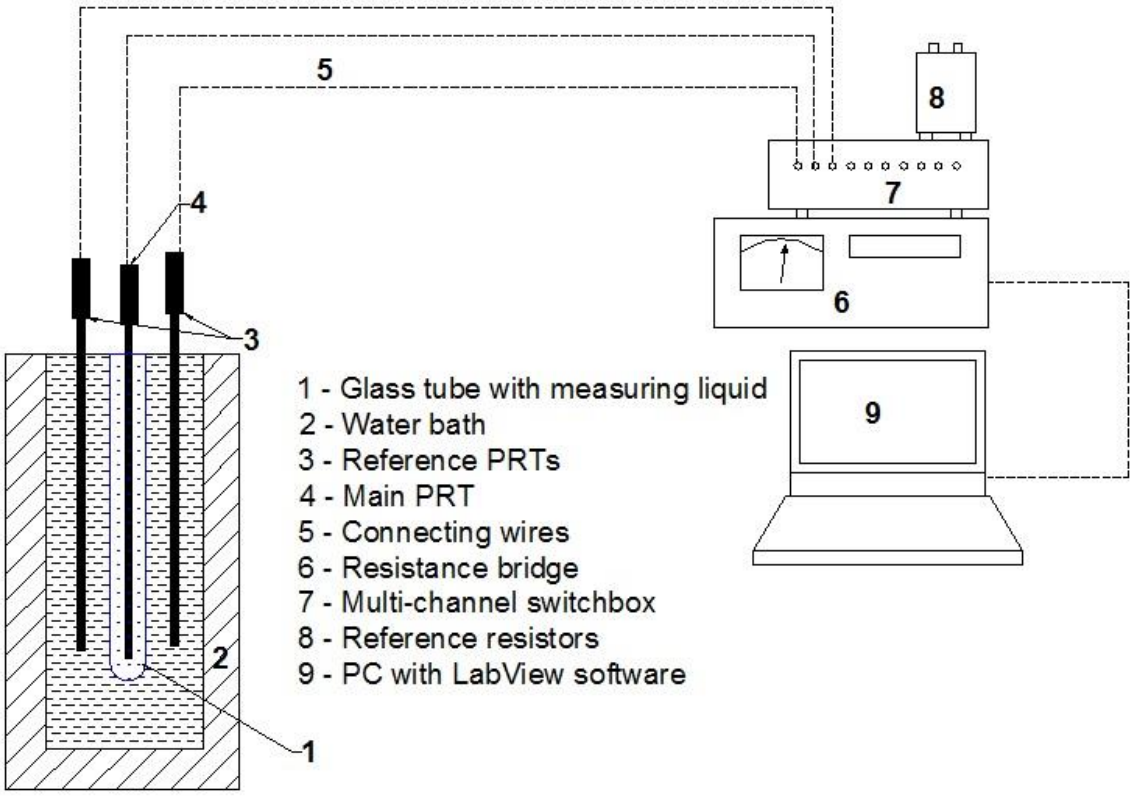

Figure 17. Measurement setup schematic

A borosilicate glass tube with an outside diameter of 10 mm, a wall thickness of 1 mm and a length of 400 mm was selected. There are several reasons for selecting a tube made from this material. Borosilicate glass is resistant to water, strong acids, alkali and saline solution and it is chemically inert which is important because this method was first designed to be used with highly corrosive chemicals. Furthermore, we were researching if it would be better to use a tube made from stainless steel or borosilicate glass. We have found that because of the small temperature differences between the PRT sensor and the water bath temperature it was better to use a material which had lower temperature conductivity (borosilicate glass 1.14 W/(m K) and stainless steel 16 W/(m K)). In this case, the temperature differences are relatively small and by making them even smaller it could become a problem to observe the thermal feedback of the sample liquid. Another reason for using glass was that the liquid level and the sensor position inside the tube are easily visible. To ensure that the PRT sensor is not touching the glass and that it is straight in the central position, we used plastic hollow cylinders called distancers, which were made in the mechanical workshop to fit PRT sensors. The position of the PRT sensor was assured with 2 distancers, one

placed at the top of PRT and one down near the sensor, but high enough to minimize the effect of heat conduction through plastic material.

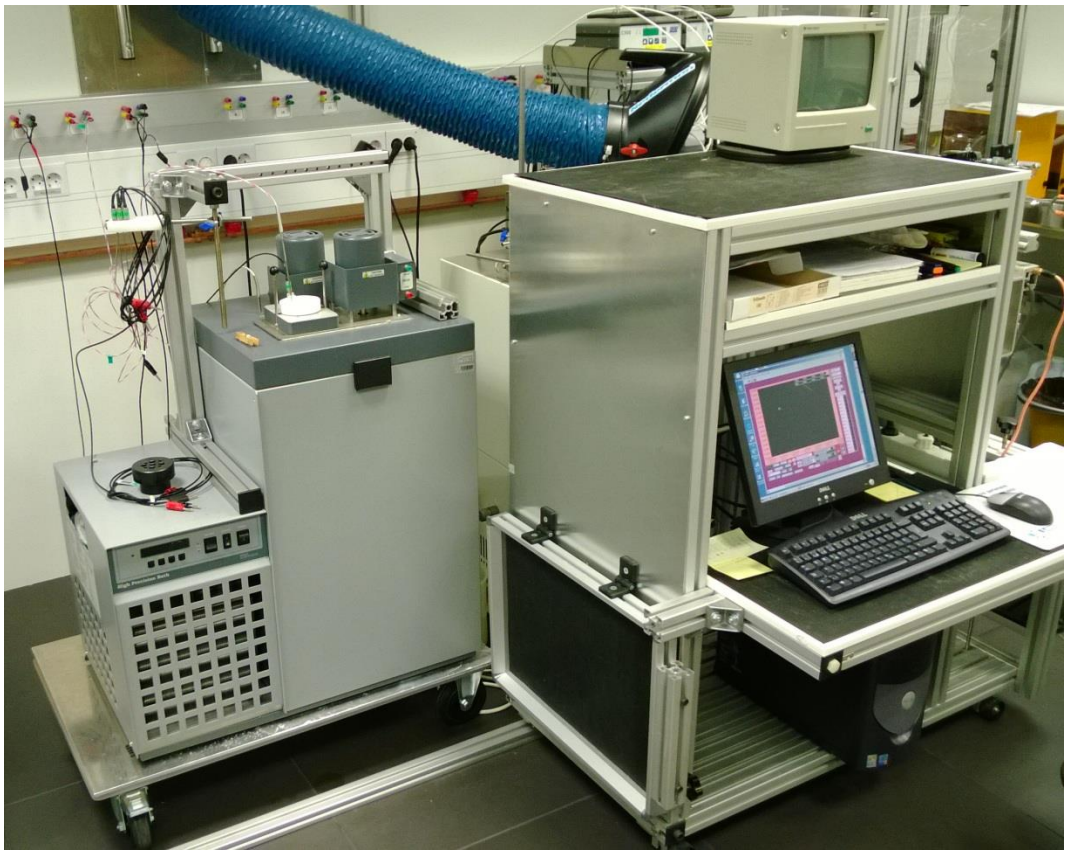

Figure 18. Measurement setup in the temperature laboratory at MIKES

With the help of distancers, the PRT was positioned in the tube filled with the sample liquid and immersed into the water bath. After adjusting the desired temperature of bath, we let it stabilize and monitored the water temperature with the reference PRTs. When we were certain that the temperature was maximally stable, we conducted measurements of the temperature in the following intervals.

- 1st check - before every measurement, the resistance bridge was left to stabilize for 20 s, and every measurement lasted 2 min with a reading every 10 s.
    - Burns 1 PRT
    - SAB PRT (+ tube, + sample liquid)
    - Burns 2 PRT
- Sample liquid measurements with SAB PRT on different currents in this order
    - 1 mA

- $\sqrt{2}$ mA
- 5 mA
- 1 mA

- 2nd check - before every measurement resistance bridge was left to stabilize for 20 s, and every measurement lasted 2 min with reading every 10 s.
  - Burns 1 PRT
  - SAB PRT (+ tube, + sample liquid)
  - Burns 2 PRT

The same procedure was applied to the reference water and other liquids. 1 mA measurement was conducted twice as a check of stability. After applying a different current we waited for some time to reach a thermal equilibrium, before collecting the temperature data. Setting the PRT currents and data collection was done with LabVIEW application developed by MIKES.

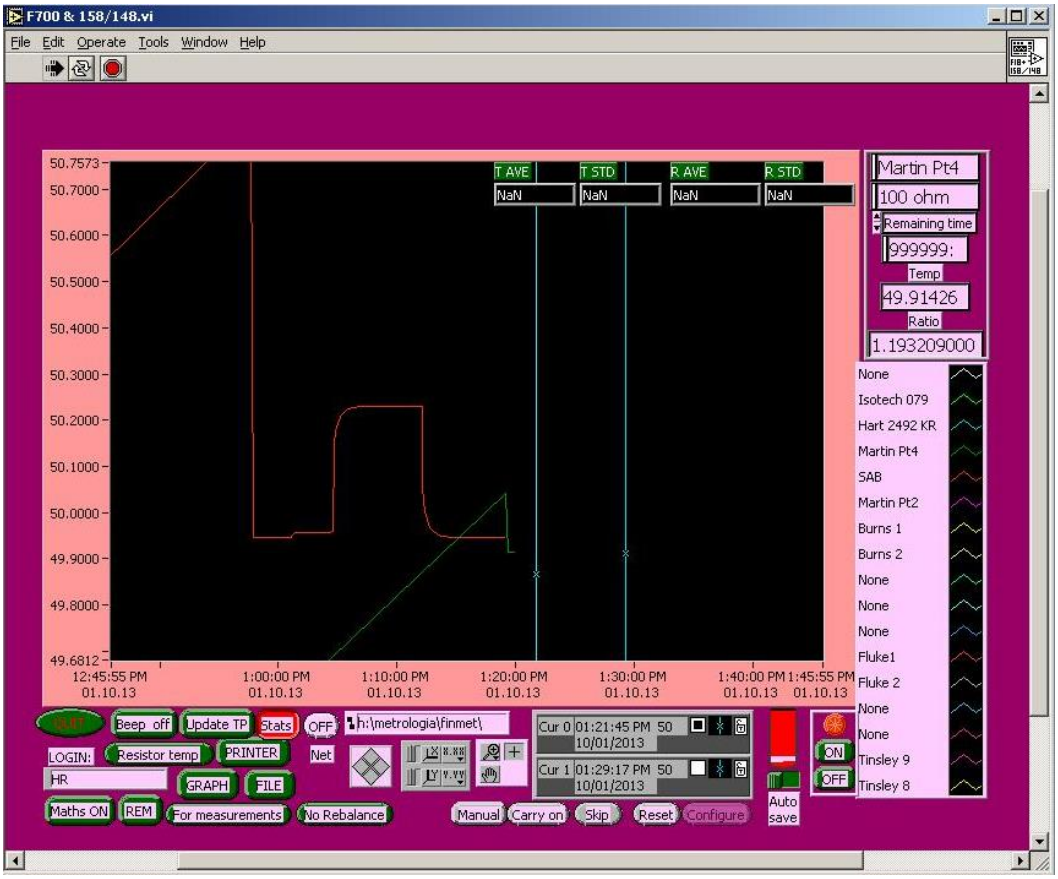

Figure 19. LabVIEW application used for data acquisition

After conducting the two measurements, one with the reference liquid and other with the liquid which thermal conductivity we are looking for, data analysis was done. To obtain the temperature

value for determining the thermal conductivity, the self-heat error was subtracted from the averaged temperature on a specific current. After repeating for other currents and on both liquids, thermal conductivity could be calculated using equation (2.12).The most accurate result should be with the largest temperature difference, in this case on currents 1 mA and 5 mA.

3.2. Results analysis

Using this method, we could directly measure only the temperature (resistance). To acquire thermal conductivity we needed to use temperature data from two different currents and two liquids and use equation (2.12).

After many measurements taken, the importance of taking the partial self-heat error into account was observed. From averaged resistance value on 5 or $\sqrt{2}$ mA current, the partial self-heat error previously measured was subtracted and temperature was calculated using fifth degree polynomial function and coefficients from calibration.

$$T = a + b \cdot R + c \cdot R^2 + d \cdot R^3 + e \cdot R^4 + f \cdot R^5 \tag{3.1}$$

Table 5. Calculated coefficients from calibration of SAB PRT

a =	4.04E+03
b =	-1.76E+02
c =	2.98E+00
d =	-2.47E-02
e =	1.03E-04
f =	-1.70E-07

Table 6. Measured temperatures, resistances and applied self-heat error over different currents in water and ethanol

		Water				Ethanol			
			SAB				SAB		
	Ref. Ther	1 mA	Sqrt(2) mA	5 mA	1 mA	1 mA	Sqrt(2) mA	5 mA	1 mA
Temp	19.91295	19.95597	19.96529	20.17105	19.95591	19.96062	19.97285	20.26009	19.9607
Resistance		107.7775	107.7811	107.861	107.7774	107.7793	107.784	107.8956	107.7793
Res. Selfheat error			0.002789	0.065102			0.002789	0.065102	
Res. After self heat		107.7775	107.7783	107.7959	107.7774	107.7793	107.7812	107.8305	107.7793
Calculated temp		19.9306	19.93273	19.97798	19.93054	19.93524	19.94027	20.06675	19.93531

By using water as a reference liquid we got these values for ethanol's thermal conductivity at 20°C:

Table 7. Calculated thermal conductivity of ethanol compared to water over different currents and PRT sensors

	Temp. difference between currents		
Ethanol	5-1 mA	5-$\sqrt{2}$ mA	$\sqrt{2}$-1 mA
SAB	0.200	0.198	0.242
Pt 4	0.191	0.191	0.197

And for ethylene glycol we got these values:

Table 8. Calculated thermal conductivity of ethylene glycol compared to water over different currents and PRT sensors

	Temp. difference between currents		
Ethylene glycol	5-1 mA	5-sqrt(2)	sqrt(2)-1mA
SAB	0.279	0.277	0.346
Pt 4	0.271	0.269	0.311

In the [Table 7. and 8.] we can see that thermal conductivity between currents 5 and 1 mA or 5 and $\sqrt{2}$ mA are the same or if not almost the same. When comparing temperatures measured between $\sqrt{2}$ and 1 mA there was a deviation in a value. We have repeated measurements many times and with different PRT sensors and we always got a deviation in thermal conductivity value with ΔT at currents $\sqrt{2}$-1 mA compared to other two current groups. We did not find reason for this deviation, but we assumed it is probably because of a small difference in current and temperature. It was decided to use only thermal conductivity calculated from 5-1 mA and 5 -$\sqrt{2}$ mA temperature difference.

3.3. Verification of the method

One of the main goals of this thesis was to prove that this method gives useful results in reality. The obvious way to validate it was to use liquids which have a known value for thermal conductivity and compare them to the values obtained from our measurements. In the [Table 9.]

we can see the reference thermal conductivity values of the liquids which we used in our experiment.

Table 9. Reference values for thermal conductivity at 20°C

Liquid	**Thermal conductivity – W/(m K)**
Water	0.598
Ethanol	0.179
Ethylene glycol	0.258

Highly purified laboratory water was used, prepared by double distillation system. The used ethanol was pure at 96.7 % and ethylene glycol more than 99%.

In our main equation (2.12) we needed to include the value of the reference liquid used, at the beginning we used only water. In the [Table 10.] we can see the difference between the measured values and the reference values when the measurand liquid is compared to water.

Table 10. Difference between measured values and reference values (reference liquid is water)

Thermometer	SAB		Pt 4	
Electric current	5-1 mA	5-$\sqrt{2}$ mA	5-1 mA	5-$\sqrt{2}$ mA
Ethanol				
Thermal conductivity	0.200	0.198	0.191	0.191
Error (%)	12%	11%	7%	7%
Ethylene glycol				
Thermal conductivity	0.279	0.277	0.271	0.269
Error (%)	8%	7%	5%	4%

We can see that the difference between the measured and the reference values depends on the PRT and currents used, although the difference is not so large in the context of measuring a liquid's thermal conductivity. It was observed from the results with ethylene glycol we got smaller error then with ethanol.

By using a numerical simulation and through experimentation, the influence of vertical heat flow through the PRT was discovered. In the mathematical model we assumed that if there was any

vertical heat flow it would be neutralized with the vertical heat flow of the other liquid measured. This theory was viable if we compared two liquids with the same thermal conductivity value. But if they were not the same, heat flows through liquid would not be the same and we would get an error in measured values. Greater the difference in thermal conductivity value, greater the error. Which meant that we had to compare liquids with closer conductivity value to minimize the error. Accordingly, what we did next was compare ethanol and ethylene glycol between each other.

Table 11. Difference between measured values and reference values (reference liquids are ethanol and ethylene glycol)

Thermometer	SAB		Pt 4	
Electric current	5-1 mA	5-$\sqrt{2}$ mA	5-1 mA	5-$\sqrt{2}$ mA
Ethylene glycol from ethanol				
Thermal conductivity	0.250	0.249	0.253	0.252
Error (%)	-3%	-3%	-2%	-2%
Ethanol from ethylene glycol				
Thermal conductivity	0.185	0.185	0.182	0.183
Error (%)	3%	3%	2%	2%

Ethanol and ethylene glycol have a much smaller difference in conductivity then when compared with water. In the [Table 11.] we can see much smaller errors then previously showed in comparison with water. Also we can observe that if the reference liquid has a lower conductivity value, the results are lower than the true value (negative error) and the other way around.

4. MEASUREMENT UNCERTAINTY

Measurement uncertainty is defined as a parameter attached to the result of measurement which describes dissipation of a value with certain probability.

Measurements are not perfect due to random errors (change in temperature, pressure or humidity, because of inexperienced measurer or imperfect device) or to systematic errors (reading the analog scale, uncertainty in value of reference standard, etc.). Measurement uncertainty is a consequence to the existence of random errors and limited possibilities to correct systematic errors.

4.1. Sources of measurement uncertainty

In this work we described the following sources of uncertainty:

- Instability of electric current
- Stability of water bath temperature
- Length measurement (radius of tube and PRT)
- Reference liquid and glass tube properties
- Measured temperature difference between two currents in the same liquid
- Heat flow difference between two liquids of diverse thermal conductivity

4.2. Sensitivity coefficients

To calculate the sensitivity coefficients our main equation (2.12) for thermal conductivity was used. To estimate the sensitivity coefficient several derivatives were calculated, derived by each quantity in the equation.

Sensitivity coefficients for:

Inner radius of glass tube $$\frac{\partial \lambda_M}{\partial r_2} = -\frac{\Delta T_R \lambda_G \lambda_R^2 (\Delta T_R - \Delta T_M)\left(ln\frac{r_3}{r_2} + ln\frac{r_2}{r_1} \right)}{r_2 \left[\lambda_R (\Delta T_R - \Delta T_M) ln\frac{r_3}{r_2} - \lambda_G \Delta T_M \, ln\frac{r_2}{r_1} \right]^2} \tag{4.1}$$

Outer radius of glass tube $$\frac{\partial \lambda_M}{\partial r_3} = \frac{\Delta T_R \lambda_G \lambda_R^2 (\Delta T_R - \Delta T_M) \cdot ln\frac{r_2}{r_1}}{r_3 \left[\lambda_R (\Delta T_R - \Delta T_M) ln\frac{r_3}{r_2} - \lambda_G \Delta T_M \, ln\frac{r_2}{r_1} \right]^2} \tag{4.2}$$

Radius of PRT sensor $$\frac{\partial \lambda_M}{\partial r_1} = \frac{\Delta T_R \lambda_G \lambda_R^2 (\Delta T_R - \Delta T_M) \cdot ln\frac{r_3}{r_2}}{r_1 \left[\lambda_R (\Delta T_R - \Delta T_M) ln\frac{r_3}{r_2} - \lambda_G \Delta T_M \, ln\frac{r_2}{r_1} \right]^2} \tag{4.3}$$

Thermal conductivity of glass tube $$\frac{\partial \lambda_M}{\partial \lambda_G} = -\frac{\Delta T_R \lambda_R^2 (\Delta T_R - \Delta T_M) \cdot ln\frac{r_3}{r_2} \cdot ln\frac{r_2}{r_1}}{\left[\lambda_R (\Delta T_R - \Delta T_M) ln\frac{r_3}{r_2} - \lambda_G \Delta T_M \, ln\frac{r_2}{r_1} \right]^2} \tag{4.4}$$

Thermal conductivity of measurand liquid $$\frac{\partial \lambda_M}{\partial \lambda_R} = \frac{\Delta T_R \lambda_G^2 \Delta T_M \cdot \left(ln\frac{r_2}{r_1} \right)^2}{\left[\lambda_R (\Delta T_R - \Delta T_M) ln\frac{r_3}{r_2} - \lambda_G \Delta T_M \, ln\frac{r_2}{r_1} \right]^2} \tag{4.5}$$

Reference liquid temperature difference $$\frac{\partial \lambda_M}{\partial \Delta T_R} = \frac{\lambda_G \Delta T_M \lambda_R \, ln\frac{r_2}{r_1} \cdot \left(\lambda_G \, ln\frac{r_2}{r_1} + \lambda_R \, ln\frac{r_3}{r_2} \right)}{\left[\lambda_R (\Delta T_R - \Delta T_M) ln\frac{r_3}{r_2} - \lambda_G \Delta T_M \, ln\frac{r_2}{r_1} \right]^2} \tag{4.6}$$

Measurand liquid temperature difference $\frac{\partial \lambda_M}{\partial \Delta T_M} = -\frac{\lambda_G \Delta T_R \lambda_R \ln\frac{r_2}{r_1} \cdot \left(\lambda_G \ln\frac{r_2}{r_1} + \lambda_R \ln\frac{r_3}{r_2} \right)}{\left[\lambda_R (\Delta T_R - \Delta T_M) \ln\frac{r_3}{r_2} - \lambda_G \Delta T_M \ln\frac{r_2}{r_1} \right]^2}$ (4.7)

This sensitivity coefficients are only the ones from the main equation and it was still necessary to find electric current and heat flow difference coefficients. After these were included, in order to finish the report for measurement uncertainty, it was necessary to estimate standard uncertainty for each of the uncertainty sources listed above.

4.2.1. Electric current

Uncertainty was taken from the specifications of the resistance thermometry bridge and calculated with highest current used (5 mA) and equals to ±1%. Standard uncertainty is, where ΔI_{MAX} is 1% of highest current used ($I = 5mA$)

$$u(C) = \frac{\Delta I_{MAX}}{I\sqrt{3}} \tag{4.8}$$

To calculate sensitivity coefficient we added C constant into our model's main equation.

$$\Delta\Phi_{thermal} = C\Delta\Phi_E = C \cdot R(I_1^2 - I_2^2) \tag{4.9}$$

By inserting this to main equation (2.12) with indexes 1 and 2 for each liquid measured we got

$$\lambda_M = \frac{\ln\frac{r_2}{r_1}}{\frac{C_2}{C_1}\frac{t_{M1C} - t_{M2C}}{t_{R1C} - t_{R2C}}\left(\frac{1}{\lambda_R}\ln\frac{r_2}{r_1} + \frac{1}{\lambda_G}\ln\frac{r_3}{r_2} \right) - \frac{1}{\lambda_G}\ln\frac{r_3}{r_2}} \tag{4.10}$$

C_2 and C_1 values are 1 but they still had uncertainty in them.

By deriving λ_M with $\frac{C_2}{C_1}$ we got sensitivity coefficient

$$\frac{\partial \lambda_M}{\partial \frac{C_2}{C_1}} = \Delta T_M \frac{\partial \lambda_M}{\partial \Delta T_M}. \tag{4.11}$$

4.2.2. Stability of water bath

For the reference thermometer we used Burns PRT immersed in bath water. Before and after each measurement the bath temperature was collected with the PRT for 2 minutes in 10 seconds intervals. From those values standard uncertainty was calculated. And as the temperature stability of water bath influences the liquid temperature difference, higher sensitivity coefficient was picked and multiplied with standard uncertainty. In this case, it was the coefficient from the reference liquid (water).

4.2.3. Length measurement

As it was assumed, the length measurements in this method are not of crucial importance, as it is seen from the values for the sensitivity coefficient. In standard uncertainty calculation we only included type A uncertainty of radius and thickness (repeated measurements) and uncertainty because of the resolution of the digital caliper device. These two were combined together. The digital caliper has the smallest significant digit of 0.01.

$$u(res) = \frac{0.01}{\sqrt{12}} \tag{4.12}$$

The combined uncertainties were then multiplied with the appropriate sensitivity coefficient.

4.2.4. Reference liquid and glass tube properties

Glass tube (borosilicate glass) thermal conductivity was taken from various sources (thermodynamic tables and manufacturer's catalog) and Type A standard uncertainty was calculated.

On the other hand, reference water thermal conductivity was compared to the conductivity of tap water. The reference water was produced with distillation from tap water so in the worst case scenario it would have the conductivity of tap water. Also, it was calculated as type A uncertainty with normal distribution.

4.2.5. Measured temperature difference between two currents in same liquid

The accuracy of the temperature difference measurement between two currents was limited by:

- stability of temperature at single current
- repeatability of temperature at same current in one setup
- difference in temperature rise from 1 mA to 5 mA in repeated setup and measurement
- linearity of temperature dependence in calibrated fitting compared to standard fitting by IEC 60751
- uncertainty of PRT's self-heat measurement

Uncertainty of temperature stability at single current was calculated by combining two type A uncertainties, which were calculated from the temperature readings (15 to 25 points)

In the measurement procedure we measured temperatures on different currents in this order: 1 mA, $\sqrt{2}$ mA, 5 mA and again 1 mA for check-up. To determine uncertainty in repeatability of temperature at the same current, the difference between average temperatures at 1 mA was calculated and uniform distribution was assumed.

To calculate standard uncertainty of temperature rise when measured with 1 mA and 5 mA, temperature values from two separate measurements were used and uniform distribution were assumed.

The PRT used was calibrated by MIKES and the fifth polynomial curve fitting was calculated from the results with CurveExpert software. To check for uncertainty, Callendar–Van Dusen equation, which is cited in IEC 60751 as the international standard for PRT's resistance versus temperature function, was compared to our fitted function. The comparison was carried out by derivation of each function by resistance, by multiplying with the largest resistance value difference (1-5mA), calculating the difference between two results and applying the uniform probability density.

Fitted function $T = a_1 + a_2 R + a_3 R^2 + a_4 R^3 + a_5 R^4 + a_6 R^5$ (4.13)

Table 12. Coefficients for fifth polynomial curve fitting of calibrated PRT sensor

a_1	4041.739633
a_2	-176.38867
a_3	2.97740301
a_4	-0.02474461
a_5	0.000102708
a_6	-1.7028E-07

$$\frac{\partial T}{\partial R} = a_2 + 2a_3R + 3a_4R^2 + 4a_5R^3 + 5a_6R^4 \tag{4.14}$$

IEC 60751 function $$t = \frac{-R_0 \cdot a + \sqrt{R_0^2 \cdot a^2 - 4 \cdot R_0 \cdot b \cdot (R_0 - R)}}{2 \cdot R_0 \cdot b} \tag{4.15}$$

$$\frac{\partial T}{\partial R} = \frac{1}{\sqrt{R_0(a^2R_0 + 4b(R - R_0)}} \tag{4.16}$$

where

a	3.91E-03
b	-5.78E-07

Uncertainty in self-heat error was determined from two single self-heat error measurements, from which the difference was calculated and the uniform probability density assumed.

All the listed standard uncertainties for liquid temperature difference were added and multiplied by the calculated sensitivity coefficient. The same procedure was done for the reference and the measurand liquid.

4.2.6. Heat flow difference between two liquids of diverse thermal conductivity

As we compare two liquids in this method, the heat flow through the PRT changes. It is higher with a smaller conductivity of liquid. To assume uncertainty we decided to use data from the measurement of tap water with comparison to distilled water and ethylene glycol.

λ_X reference value for T. cond. of tap water

λ_{Xm1} is measured T. cond. of tap water compared to distilled water

λ_{Xm2} is measured T. cond. of tap water compared to ethylene glycol

λ_{R1} reference value of T. cond. of distilled water

λ_{R2} reference value of T. cond. of ethylene glycol

$$\Delta\lambda = c(\lambda_X - \lambda_R) \tag{4.17}$$

where $\Delta\lambda$ was added to model equation (2.12) even though value was zero it still had some uncertainty which we needed to address.

Where t. cond. from one measurement could be subtracted from another to get value for *c*.

Assuming that $\Delta\lambda_1 - \Delta\lambda_2 \approx \lambda_{XM1} - \lambda_{XM2}$ we get:

$$\Delta\lambda_1 - \Delta\lambda_2 = c\left[(\lambda_X - \lambda_{R1}) - (\lambda_X - \lambda_{R2})\right] \tag{4.18}$$

Which gave us c_m calculated from maximum T. cond. difference.

$$c_m = \frac{\lambda_{XM1} - \lambda_{XM2}}{\lambda_{R2} - \lambda_{R1}} \tag{4.19}$$

By assuming rectangular distribution we got standard uncertainty for c

$$u(c) = \frac{c_m}{\sqrt{3}} \tag{4.20}$$

from which we could calculate standard uncertainty for difference in t. cond. between two liquids.

$$u(\Delta\lambda) = u(c)(\lambda_X - \lambda_R) \tag{4.21}$$

Sensitivity coefficient is 1 as $\frac{\partial\lambda_L}{\partial\Delta\lambda} = 1$ (4.22)

4.3.Uncertainty budget

After calculating all of the sensitivity coefficients and standard uncertainties [Table 13.] for uncertainty budget was created.

From the uncertainty budget it can be seen that the most influential component is uncertainty because of difference in a liquid's thermal conductivity. However for uncertainty budget we have used worst case, if we would compare liquids of much closer thermal conductivity, uncertainty contribution would be substantially lower. For example, in the case of our uncertainty budget we have compared the tap water with the ethylene glycol and uncertainty contribution is equal to 0.031731 W/(m·K). If we compared tap water with distilled water we would have got uncertainty contribution of 0.000637 W/(m·K), which is substantially lower than in shown uncertainty budget.

Uncertainty budget shows that comparative self-heating method for measuring the thermal conductivity of liquids is a competent method. However quality of the method depends on the chosen reference liquid.

i	Quantity, Xi Description	Estimate, xi Value	unit	Standard unc., u(xi) Value	unit	Probability distribution	Sensitivity coeff., ci Value	unit	Uncertainty contribution, ui Value	unit
1	electric current	5×10^{-3}	A	0.005773503	A	Rectangular	-0.216623	W/(mKA)	-0.001251	W/(mK)
2	Stability of water bath	19.9130	°C	5.51776E-05	°C	Rectangular	4.239845	W/(mK°C)	0.000234	W/(mK)
3	inner radius of the tube	0.00396333	m	3.33333E-06	m	Normal	0.020433	W/(m^2K)	0.000000	W/(mK)
4	radius of PRT	0.001458	m	7.40495E-06	m	Normal	-0.01017	W/(m^2K)	0.000000	W/(mK)
5	outer radius of the tube	0.00493778	m	5.83994E-06	m	Normal	-0.013223	W/(m^2K)	0.000000	W/(mK)
6	T.conductivity of glass	1.14	W/(mK)	0.005773503	W/(mK)	Rectangular	0.0129573	-	0.000075	W/(mK)
7	T.conductivity of water	0.598	W/(mK)	0.003464102	W/(mK)	Rectangular	0.3227821	-	0.001118	W/(mK)
8	Ref. Liquid temp. difference	0.2188	°C	0.0023176	°C	Rectangular	4.239845	W/(mK°C)	0.009826	W/(mK)
9	Meas. Liquid temp.differenc	0.3046	°C	0.003172798	°C	Rectangular	-1.586019	W/(mK°C)	-0.005032	W/(mK)
10	uncertainty because of difference in liquids Tcond		W/(mK)	0.031731119	W/(mK)	Rectangular	1	W/(mK)	0.031731	W/(mK)
						Combined standard uncertainty:			0.0336	W/(mK)
						Expanded uncertainty:			0.0673	W/(mK)

Table 13. Uncertainty budget

5. CONCLUSION

This work investigated a method for determining the thermal conductivity of liquids with the use of self-heating of platinum resistance thermometers (PRT). The measurement setup was developed and was optimized with a numerical simulation. The goal of the study was to validate the method by comparing measurement results to the reference values for used liquids and to improve the method so the difference in those values would be minimal.

During the first measurements, the setup showed significant errors, when comparing the results to the reference values. We studied and measured the influence of the self-heating error on the results and included of the correction into the analysis. Further investigation showed a great impact of the difference in thermal conductivity between the measurand and the reference liquid. This means that a more resistant liquid causes a reduced heat flow through the liquid, as more heat goes vertically through the PRT. Therefore, the effect of the vertical heat flow does not cancel out, when compared to a liquid of different thermal conductivity. To reduce this error, liquids of similar thermal conductivity should be used.

Due to the lack of time, measurements on higher temperatures have not been properly investigated. Future work should also include a categorization according to reference liquid, where the measurand liquid would be compared to the closest reference liquid. In addition, more experiments should be done to determine how accurately we can measure thermal conductivity considering the difference in conductivity between the measurand and the reference liquid.

The comparative self-heating method for measuring the thermal conductivity of liquids is a method that can be easily done in every temperature laboratory which is equipped with a high stability temperature bath, without acquiring any additional equipment. This method also enables to determine the thermal conductivity of any liquid whose temperature could be measured with a platinum resistance thermometer (PRT).

The work on this thesis has helped me expand my knowledge and gain experience in the fields of metrology, thermodynamics, numerical simulations and last but not least, improve my knowledge of the English language. All of this will surely help me with rest of my studies and my future career.

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APPENDICES

I. CD-R disc